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TRI-SERVICE CONFERENCE ON CORROSION



21-23 JUNE 1994

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ORLANDO, FLORIDA**

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Army Research Office Programs In Beam Technology and Surface Engineering

Robert R. Reeber
Materials Engineer
Army Research Office
Research Triangle Park, NC 27709

The objective here is to provide some idea of needs and opportunities for future research with potential for providing new capabilities for Army systems. The technical objectives of the program are 1. to discover the atomic, molecular and macroscopic processes governing deterioration and adhesion of materials, 2. to provide improved materials stability and longer term performance capability for Army systems, and 3. to educate the next generation of skilled scientists in areas of Army research opportunities and needs.

Two principal thrust areas, (1) Beam Technology and Surface Modification and (2) Non-Destructive Characterization of Materials and Processes, are the templates for fulfilling the technical objectives of the program. New directions in nondestructive characterization, adhesion, non-equilibrium processing of refractory materials, ultrastrong laminates, green processing of corrosion resistant coatings and superhard coatings will be reviewed.

Research at the University of Wisconsin, Milwaukee (Carolyn Aita); has provided a characterization scheme (metastable phase maps) for refractory metal oxide sputter depositions. These results have depended on careful spectroscopic plasma characterization and determination of the crystallinity of films with x-ray, XPS and other methods. The University of Michigan (Bilello, Yalisove and Srolovitz) refractory metals laminates project where synchrotron topography and double crystal diffractometry techniques and theory are being applied to monitor and predict residual stresses and properties of nanolaminate materials.

A current program in chemical analysis with low and medium energy ion beams is underway at Vanderbilt University (Robert Weller). A new form of backscattering spectrometry using medium energy ions and time-of-flight detection has been developed that is particularly useful for characterizing surfaces and thin films. Currently some scaleup of the results is being accomplished with the cooperation of Semitech and Sandia National Laboratory.

A. Chemical/Biological Defense:

Previous work at the University of Connecticut, Koberstein, in the mid to late 1980's was cofunded by the National Science Foundation and related to surface tension measurements of polymer blends. At the same time at Cornell Kramer began seminal work to measure true diffusion coefficients of organics in polymer glasses with Rutherford Back-Scattering Spectrometry. After this work completed new efforts applying positron annihilation methods to polymers were started and are continuing. Their aim is to determine polymer free volume and its relationship to aging and transport in polymers (Case Western Reserve, McGervey, Simha and Jamieson).

B. Surface Modification/Beam Technology:

Although initially work was aimed at identifying unique properties of beam-treated materials, a growing awareness arose concerning environmental problems with plating wastes and the chemical solutions required for routine coating. This caused a

second look at what alternates were available. Some directions were identified that potentially could reduce the costs of the new technology. Lawrence Berkeley Laboratory's Ian Brown, an innovator in high current sources for implantation, was cofunded with the Office of Naval Research to further develop his technology. University of Wisconsin-Madison (John Conrad), has been evaluating the potential of Plasma Ion Implantation (PSII). The Madison group has had continuing transfers of technology to industry (Kearfoot-Singer) for space bearings, the auto industry and direct interactions with Army organizations ie. Corpus Christi Army Depot, Army Materials Technology Laboratory and Rock Island Arsenal. Their method permits non-line-of-sight implantation with relatively uniform doses.

C. Adhesion and Adhesives:

The previous sections as they relate to bonding and coating technology have already touched on some of the approaches to improved adhesion. A new STM effort addressing ceramic-metal bond integrity is ongoing with Arizona State (Ig Tsong). At Cornell, Ed Kramer is applying fracture mechanics and neutron reflectivity measurements to understand polymer/glass interface/interphase chemistry and improve bonding strengths in composites and other systems. Problems relating to effects of adhesive tackifiers are being addressed at the University of Akron and imaging of adhesive bonds is being attempted with electron holographic techniques at Stevens Institute of Technology.

D. Non-destructive Evaluation:

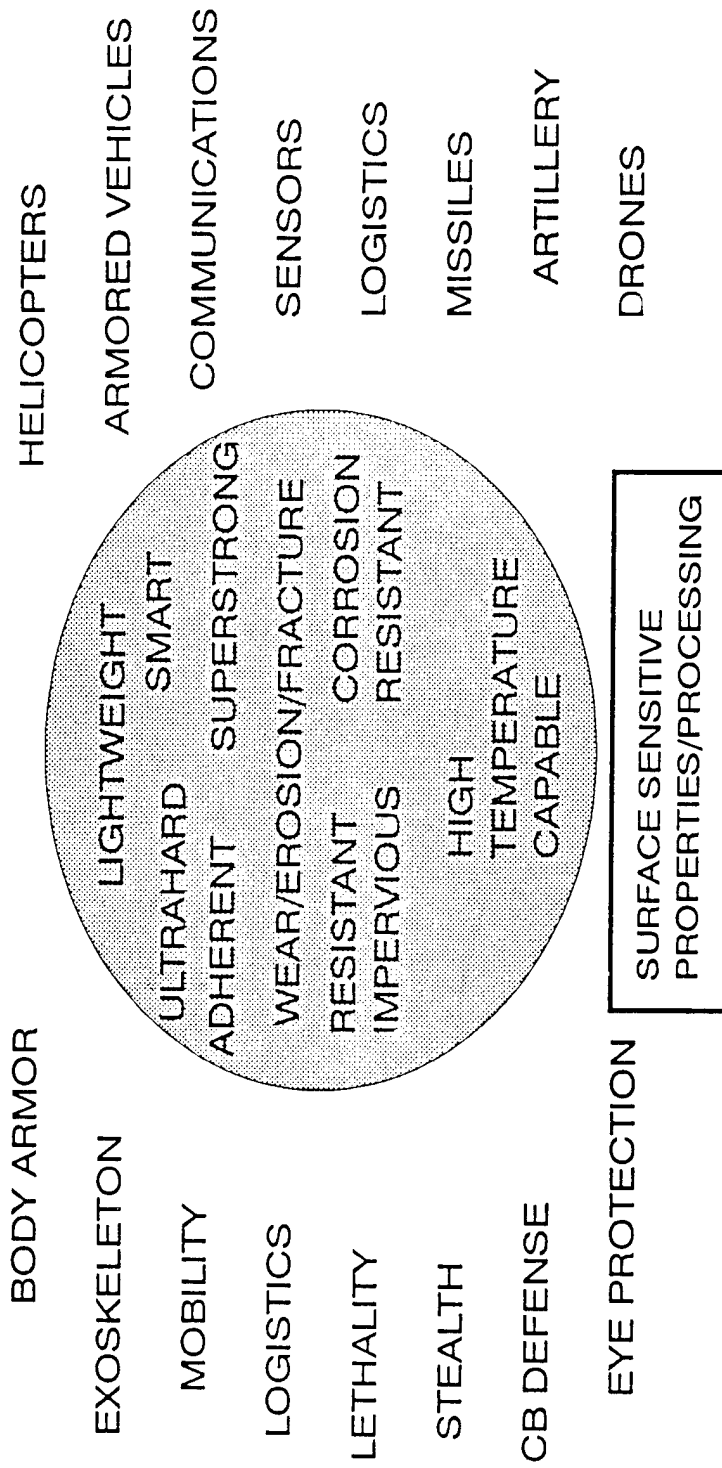
The strong subfield emphasis on materials characterization as reviewed above (hydrogen analysis, STM, laser diagnostics etc.) is included in the non-destructive characterization area. An ongoing program in the area is being carried out at the University of Houston (Salama) with the cooperation of the German Fraunhofer Institute for Non-Destructive Analysis in Saarbrücken. Here metal matrix composite third order elastic constants are being measured as a function of temperature. The results are useful in formulating mechanical equations of state for these materials. Additionally, several new small business programs have

been initiated addressing NDE needs in chemical biological materials.

I. New Needs and Directions:

The Army of the next century will require greater mobility, less reliance on logistics, and the ability to project a strong force quickly into a potential trouble spot. Such requirements can be translated into lighter weight systems and increased reliability. Higher temperature/pressure operations lead to increased efficiency but also increased stresses on equipment and munitions. New materials including lighter weight ceramic engines, a range of composite materials, graded coatings, and new polymers/elastomers will be required. Novel hard materials such as CVD diamond and cubic boron nitride are already being considered for unusual thermal and wear resistant applications. Smart coatings that provide stealth effects (neural control of color and emissivity), decontamination capabilities, self repair etc. are within the realm of possibility. New non-destructive techniques are required both to assess remaining system life and to provide in-situ monitoring of quality manufacturing. Additional research will be required to improve tribological properties of ceramics. Coatings and camouflage for polymers and polymer composites will have increasing importance. All new materials and systems processing will have to respond to increasing requirements for environmentally benign processing and recyclability. Since systems performance can often be significantly accelerated by technical breakthroughs, it is difficult to say what else to expect. Our ability to construct and characterize materials at the nanolevel will certainly reap future basic research dividends, many of which are now unforeseen.

ARMY APPLICATIONS



DEGRADATION, REACTIVITY & PROTECTION

I. BEAM TECHNOLOGY/SURFACE MODIFICATION

	FY 93 (CORE) (ALT)	FY94 (CORE) (ALT)
ION/LASER	117 351	89 0
NANOLAMINATES	145 600	114 500 e
ADHESION/SMART/GREEN	273 156	232 7.98 e
OTHER		50

II. NONDESTRUCTIVE CHARACTERIZATION

ADHESION/INTERFACES	263 0	292 0
INSERVICE	109 141	198 247
INSITU PROCESSING	86 434	59 250
TOTALS	993 1682	984 1845

BEAM PROCESSING OF MATERIALS

ATOMIC LEVEL SURFACE TREATMENT

METHODS:

- LASERS
- ION IMPLANTATION
- ION BEAM ENHANCED DEPOSITION
- PLASMA SPUTTERING
- CVD - MOCVD - MBE
- PLASMA SOURCE ION IMPLANTATION
- ELECTRON BEAM TREATMENTS

EFFECTS:

- SURFACE ZONE REFINEMENT
- MORPHOLOGY CHANGES
- AMORPHIZATION
- SURFACE MIXING
- PLANARIZE SURFACE
- ALLOYING FROM GAS & PREDEPOSITED LAYERS
- IMPROVED ADHESION
- IMPROVED CORROSION RESISTANCE

ARMY RESEARCH THRUST



01 MATERIALS SCIENCE
SUBAREA: STRUCTURAL MATERIALS
BEAM ENGINEERING/SURFACE MODIFICATION

MAJOR PERFORMERS

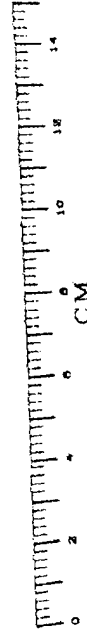
- UNIVERSITY OF CONNECTICUT
- UNIVERSITY OF WISCONSIN, MADISON
- CORNELL UNIVERSITY
- UNIVERSITY OF MICHIGAN
- BROOKHAVEN NATIONAL LAB
- IMPLANT SCIENCES, INC

ARMY RELEVANCE:

- FIRE SUPPORT, MOBILITY, AVIATION, SOLDIER

RECENT ACCOMPLISHMENTS:

- TWO IR100 AWARDS
- SUPERSTRONG NANOLAMINATES
- HIGH TEMPERATURE AL COATING
- WEAR RESISTANT CrN COATINGS
- CHROMATE-FREE CONVERSION COATINGS



MINIATURE PLASMA GUN

EXAMPLES OF RECENT TRANSITIONS TO ARMY, DoD, OR PRIVATE SECTOR PROGRAMS:

- AUTO FASTENER CONVERSION COATING TRANSFERRED TO TRW/CALLUMET/ RDEC/TTCP
- LONG ISLAND LIGHTING CO IS TESTING HIGH TEMPERATURE AL COATING FOR HEAT EXCHANGERS
- GM/LASL/UNIVERSITY OF WISCONSIN, CRDA FORMED TO UTILIZE PLASMA SOURCE ION IMPLANTATION

NONDESTRUCTIVE CHARACTERIZATION OF COATINGS (WHITE, UNIV. MO. - COLUMBIA & MANSFELD, USC)

• ZINC PHOSPHATE CONVERSION COATINGS

	MORPHOLOGY	CHEMISTRY
MODIFIED*	5-10 MICRON GRAINS	ZnPHOSPHATEDIHYDRATE
UNMODIFIED	10-20 MICRON GRAINS	ZnPHOSPHATEDIHYDRATE
*("WAVY" AND LESS ANGULAR THAN UNMODIFIED)		

• CERIUM-BASED ALUMINUM PROTECTIVE COATINGS

CHLORIDE-RESISTANT COATINGS

CERIUM CONCENTRATIONS - AT LOCAL CHEMICALLY ACTIVE REGIONS

RESULTS - MINIMAL PITTING OR LOCALIZED CORROSION

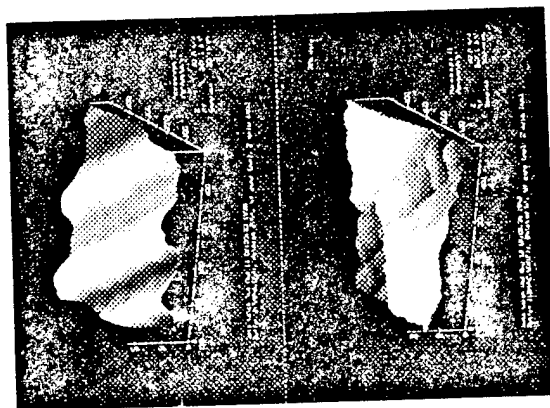
• ALUMINUM/SiC METAL MATRIX COMPOSITES

RAMAN & MICRORAMAN SPECTROSCOPY

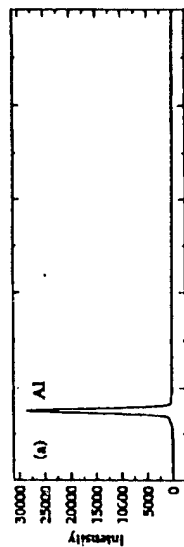
MODIFIED INTERFACES - SILICON CONTAMINATION

UNMODIFIED (PRISTINE) - SiC - ALUMINUM

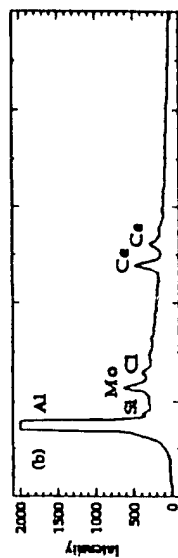
ZINC PHOSPHATE COATING MORPHOLOGY



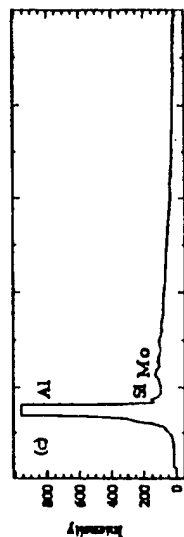
ENERGY DISPERSIVE X-RAY ANALYSIS AL 6061-T6 SURFACES (WHITE-UNIV. MO, COLUMBIA)



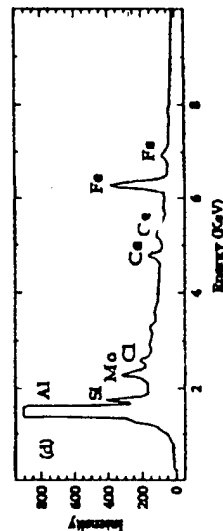
"PRISTINE"



CERIDE-TREATED
CERMIUM-RICH LOCAL REGION



CERIDE TREATED-MAJOR AREAS



CERIDE-TREATED
CERMIUM-RICH LOCAL REGION

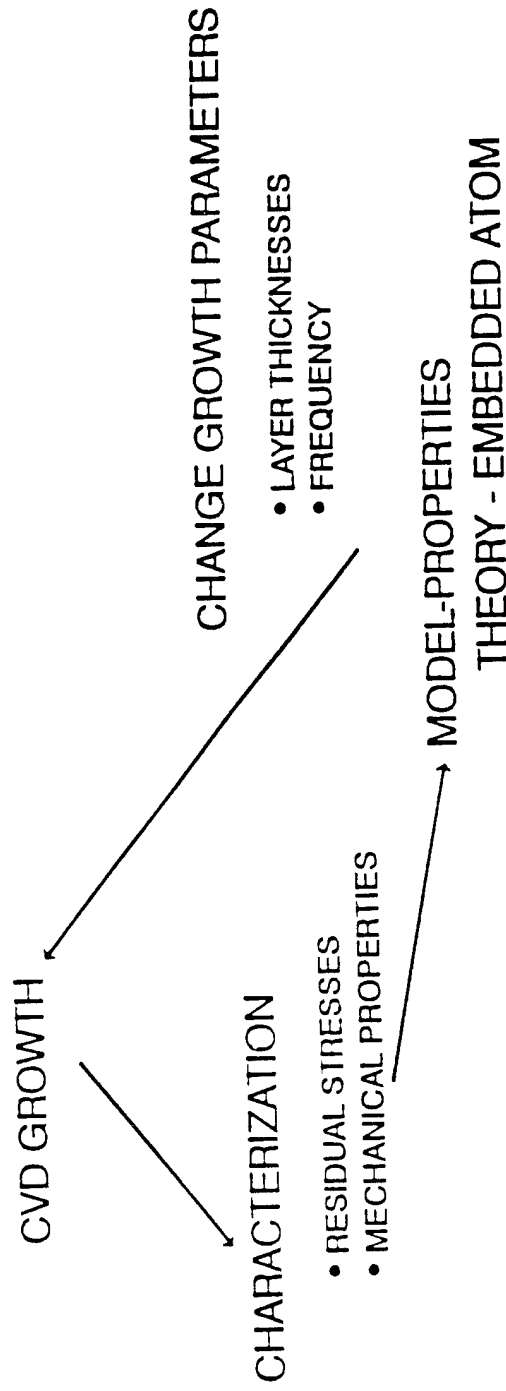
POTENTIAL: IMPROVED PITTING/LOCALIZED CORROSION RESISTANCE

TRANSFER: SAMPLES PROVIDED BY ONR PROJECT

REFRACTORY COATINGS

(BILELLO, YALISOVE, SROLOVITZ - UNIV. MICHIGAN)

METAL - METAL NANOLAMINATES



TUNGSTEN - MOLYBDENUM

APPLICATIONS

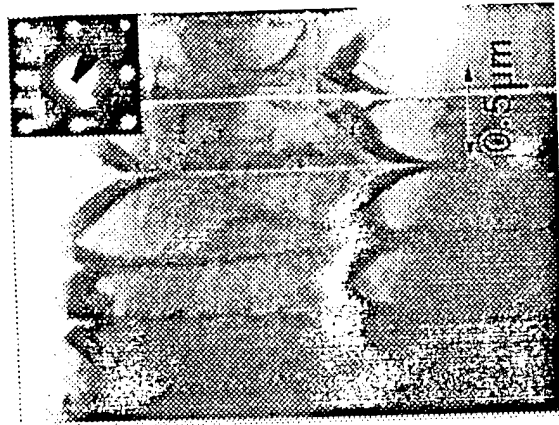
HIGH TEMPERATURE ENGINES
SUPERSTRONG MATERIALS

TUNGSTEN - MOLYBDENUM

APPLICATIONS

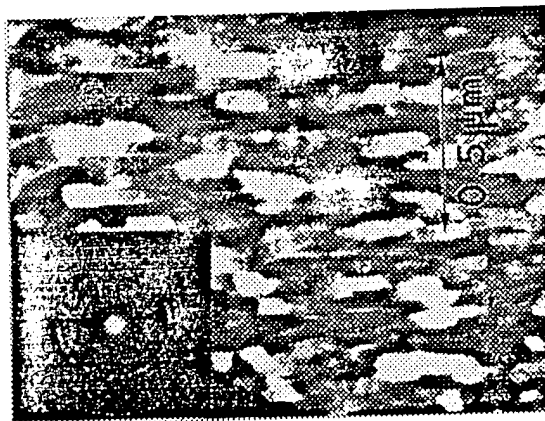
HIGH TEMPERATURE ENGINES
SUPERSTRONG MATERIALS

NANOLAMINATES
(UNIVERSITY OF MICHIGAN)



BRIGHT FIELD

BRIGHT - MO TOUGHENING LAYERS
DARK - MO/W STRENGTHENING LAYERS



DARK FIELD

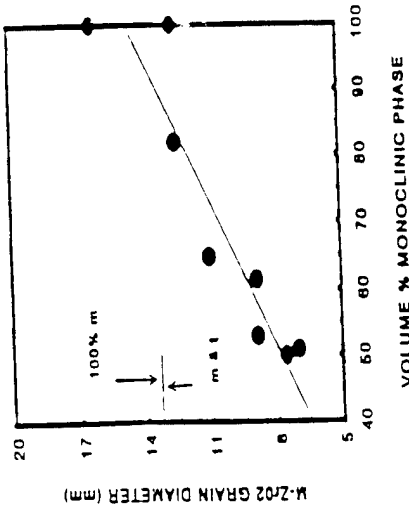
BRIGHT - INDIVIDUAL GRAINS OR GROUPS OF
GRAINS WITH SIMILAR ORIENT. 15° SECTOR OF MO
(110) RING.

TEM MICROGRAPHS

REFRACTORY COATINGS

C. AITA - UNIVERSITY OF WISCONSIN, MILWAUKEE

Zirconia Phase Distribution
(111) Monoclinic



APPROACH:

- MONITOR SPUTTER CHEMISTRY (TRANSITION METAL OXIDES, NITRIDES & OXYNITRIDES)
- MONITOR CATHODE VOLTAGE
- STRUCTURAL CHARACTERIZATION (ORDER-DISORDER)
- STRUCTURAL/MORPHOLOGY CONTROL

OBJECTIVE:

UNDERSTAND INTERRELATIONSHIPS

- PROCESS PARAMETERS
- GROWTH ENVIRONMENT
- FILM PROPERTIES

PAYOFFS:

SCIENCE

- IMPROVED COATING TECHNOLOGY
- 21 REFERRED PUBLICATIONS, 4 Ph.D, 3 MS
- 1 PATENT DISCLOSURE

ARMY

- TRANSFORMATION TOUGHENED COATINGS
- CORROSION RESISTANT HIGH TEMP. COATINGS
- NANOLAMINATE CERAMIC MATERIALS

REFRACTORY CERAMIC COATINGS

(BUNKER - IMPLANT SCIENCES INC)

APPLICATIONS:

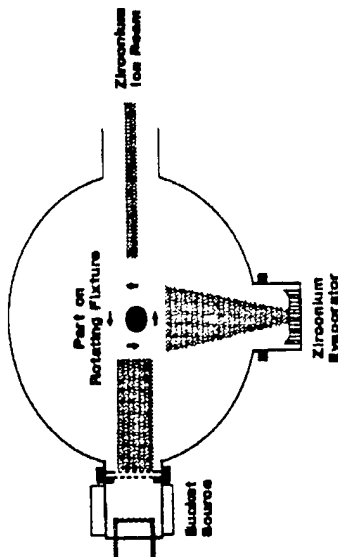
- DIESFL INJECTOR PROTECTION
- PROTHESIS (ORTHOPAEDIC DEVICES)
- CUTTING TOOLS

PROGRAM MANAGEMENT

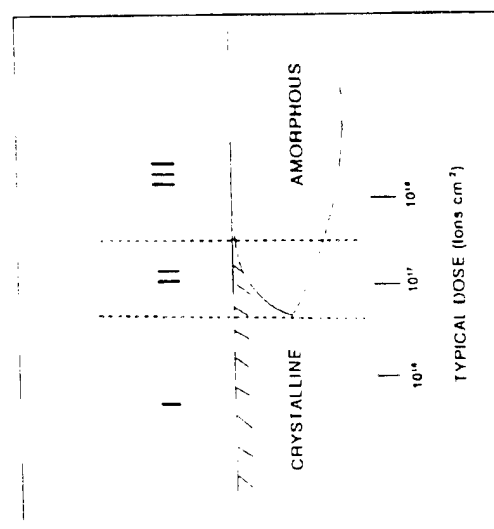
- Zr ION IMPLANTATION- OXYGEN AMBIENT
- OXYGEN IN-DIFFUSION
- C-GRADED TRANSITION LAYERS
- IBAD-TO THICKEN COATING
- TEST ZrO₂ COATINGS IN SIMULATED ENGINE ENVIRONMENTS

RESULTS:

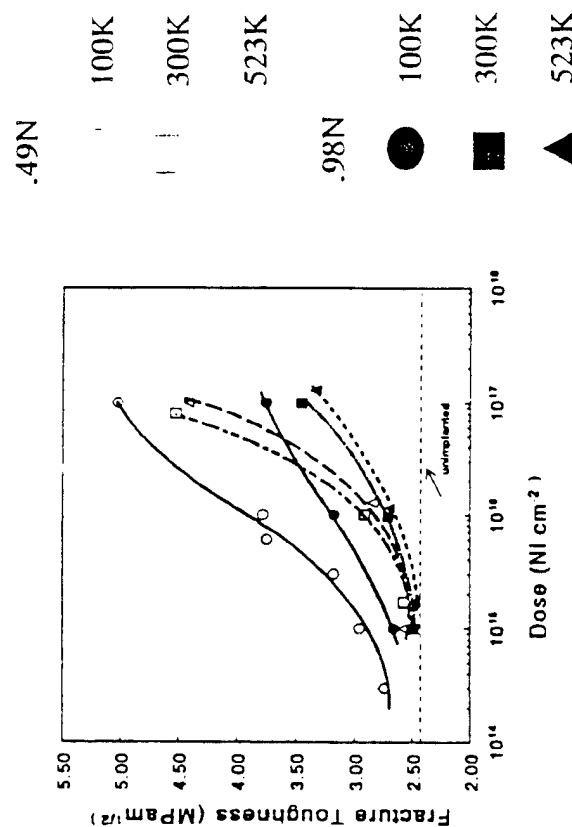
- TWO PATENT APPLICATIONS
- TECHNOLOGY INTERACTIONS
- AMBAC, INTERNATIONAL (INJECTOR), ARL-MD, BIOMEDICAL FIRMS



ION IMPLANTATION FRICTION AND WEAR



MICROSTRUCTURAL REGIMES AS
f (DOSE)
(AFTER BURNETT & PAGE)



SURFACE FRACTURE TOUGHNESS AS
f (DOSE) Ni⁺ IN ALUMINA
(HIOKI et al.)

SURFACE TREATMENTS

BORON CARBIDE

APPROACHES:

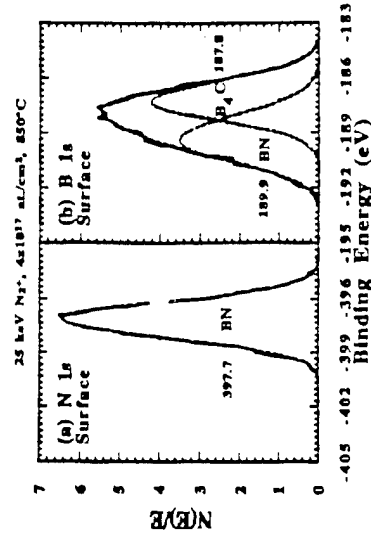
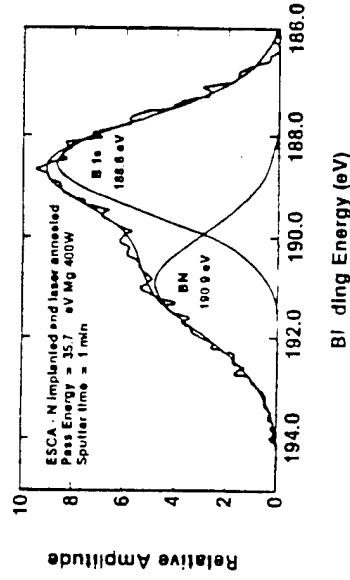
N⁺ - ION IMPLANTATION & LASER ANNEAL

N⁺ - ION IMPLANTATION AT 850°C

OBJECTIVES:

IMPROVE TRIBOLOGICAL PROPERTIES
BY INTRODUCING SOLID LUBRICANT
BN.

(REEBER & COWORKERS)
(YU & COWORKERS)



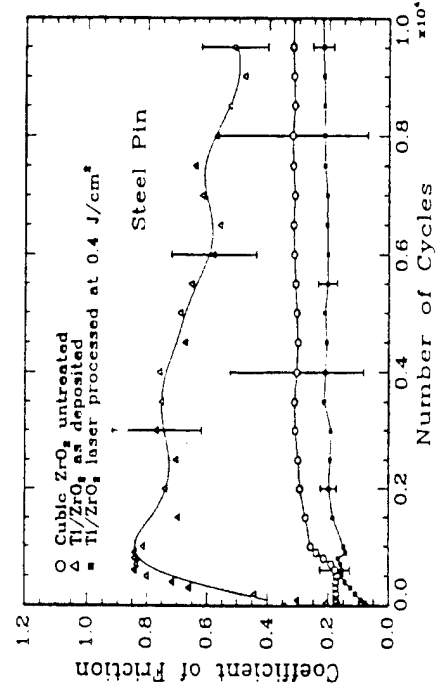
LASER MELTING TITANIUM ON ZIRCONIA (ZALESKI, JERVIS & MAYER)

OBJECTIVE:

IMPROVED TRIBOLOGICAL
PROPERTIES

APPROACH:

- NOVEL MICROSTRUCTURE
CHANGES
- SLIGHTLY SOFTER MORE
PREDICTABLE
- LOWERED FRICTION
COEFFICIENT



NON-EQUILIBRIUM PROCESSING SUPERHARD MATERIALS COATINGS

SMALL BUSINESS PROJECTS

- SI DIAMOND INC., BN, PHASE I
- IONWERKS, INC., BN, CN, PHASE II
- STRUCTURAL MATERIALS INDUSTRIES, INC., CN, PHASE I
- F.S. LAB, DIAMOND-CN, PHASE I, PHASE I
- SPACE POWER, INC, BN, PHASE I
- IMPLANT SCIENCES INC, DIAMOND, PHASE I

APPROACHES: ION/LASER/PLASMA
LIQUID INTERMEDIARY

SUMMARY

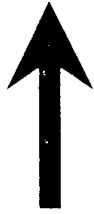
METHODS FOR IN-SITU CONTROL

- HOLOGRAPHIC
- ION BEAM ANALYSIS
- X-RAY ANALYSIS - REAL TIME
- THERMAL WAVE IMAGING
- LASER - PULSED ELECTRON GUN
- COHERENT ANTI-STOKES RAMAN (CARS)
- OTHER SPECTROSCOPIC TECHNIQUES
- ELLIPSOMETRY
- GAMMA RAY/NEUTRONS

ARMY

RESEARCH THRUST

01 MATERIALS SCIENCE SUBAREA: STRUCTURAL MATERIALS NONDESTRUCTIVE CHARACTERIZATION



MAJOR PERFORMERS

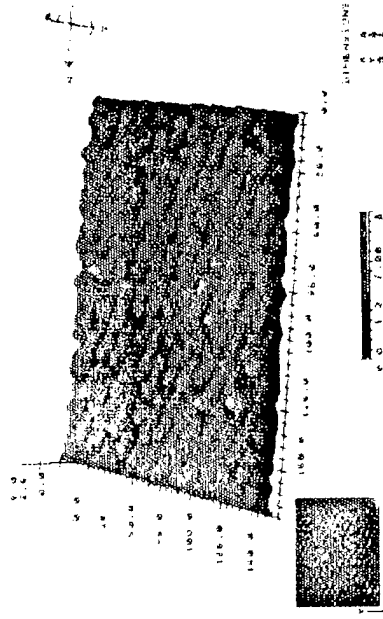
- MIT
- ARIZONA STATE UNIVERSITY
- VANDERBILT UNIVERSITY
- UNIVERSITY OF HOUSTON
- TEXAS RESEARCH INSTITUTE - AUSTIN
- IONWERKS INC.
- STEVENS INSTITUTE OF TECHNOLOGY
- CASE WESTERN RESERVE UNIVERSITY

ARMY RELEVANCE:

- COMBAT SUPPORT, CHEMICAL DEFENSE, MOBILITY, SOLDIER, CLOSE COMBAT HEAVY

RECENT ACCOMPLISHMENTS:

- REAL TIME ANALYSIS CVD DEPOSITION
- NEW NDE METHOD CBD SUIT INTEGRITY



BETA-SiC 3X3 (III) FACET

EXAMPLES OF RECENT TRANSITIONS TO ARMY, DoD, OR PRIVATE SECTOR PROGRAMS:

- SILICON WAFER₁ CONTAMINANT CHARACTERIZATION TO SEMITECH/LASL
- ION SOURCE AND REAL TIME ANALYSIS OF CVD DEPOSITION (IBM YORKTOWN)
- ELECTRON HOLOGRAPHIC CHARACTERIZATION OF ADHESIVE BONDS (ARL)

NONDESTRUCTIVE TESTING BIOLOGICAL/CHEMICAL SUITS
(BRAY-TEXAS RESEARCH INST, AUSTIN)

APPROACH:

- FLUORESCENT PENETRANT DEVELOPMENT
- PROTOTYPE TEST KIT MANUFACTURING
- ACCELERATED WEAR TESTING OF MATERIALS
- FIELD TESTING

USERS:

BATTLE LAB, ERDEC, NRDC, FIRE DEPARTMENTS CHEMICAL COMPANIES

DEGRADATION, REACTIVITY & PROTECTION TECHNOLOGY TRANSFER

UNIVERSITIES

WISCONSIN, MADISON

WISCONSIN, MILWAUKEE

STEVENS INST. TECHNOLOGY

CORNELL

CONNECTICUT

MIT

MICHIGAN

VANDERBILT

MISSOURI, COLUMBIA

USERS

ROCK ISLAND ARSENAL, CORPUS CHRISTI,
ARL-MD, CRDA WITH LOS ALAMOS & G.M.

ARDEC-BENET

ARL-MD

DOW, DUPONT ELECTRONICS, MONSANTO

ARL-ED, ARL-MD

NRDC, ARL-MD, GENERAL ELECTRIC, FORD

ARPA, PRATT & WHITNEY, MARTIN MARRIETTA

SANDIA, SEMITECH, SMALL BUSINESS

MCDONALD-DOUGLAS, ONR

DEGRADATION, REACTIVITY & PROTECTION TECHNOLOGY TRANSFER

NATIONAL LAB/SBIR

USERS

24/
BROOKHAVEN

TARDEC, TRW-FASTENERS, CALUMET, TTCR,
LONG ISLAND LIGHTING, DOE, GAS
RESEARCH INSTITUTE

LAWRENCE BERKELEY

ARDEC, IR100, EPRI, DOE

IMPLANT SCIENCES

ARL-MD, CUMMINS DIESEL, AMBAC, INT.

ION WORKS, INC

IBM YORKTOWN, COMMONWEALTH

SI DIAMOND, INC

MCDONALD DOUGLAS AIRCRAFT CO.

